Asian Journal of Chemistry; Vol. 26, No. 8 (2014), 2422-2424

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16186

Synthesis of Carbon-Encapsulated Cobalt Nanoparticles by Pyrolysis

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Received: 13 August 2013; *Accepted*: 13 December 2013; *Published online*: 15 April 2014; AJC-15040

Carbon-encapsulated magnetic cobalt nanoparticles have been produced by a low cost method using $Co(NO_3)_2$ as the cobalt precursor and starch as both reductive agent and carbon source. The structure, size distribution, phase composition, magnetic properties and oxidation resistance of the particles were investigated by transmission electron microscopy, X-ray diffraction, vibrating sample magnetometry and differential scanning calorimetry. The results show that the carbon-coated cobalt nanoparticles are spherical particles with a diameter of 20-40 nm. They are particles of core-shell structure with an cobalt core inside and an onion skin carbon layer outside, carbon layer can protect inner cobalt core from been oxidized, the hysteresis curves show that they are super paramagnetic materials. Furthermore, this method provides a simple way to prepare carbon coated nanoparticles with low cost.

Keywords: Carbon, Carbon coated nanoparticles, Pyrolysis, Magnetic.

INTRODUCTION

Carbon-encapsulated metal nanoparticles, or carbon-coated metal nanoparticles is an important nanomaterials[1]. They are new type of composite materials. These materials have a core-shell structure with a metal or metal carbide core and carbon or graphite outer layer[2,3], Due to packaged by carbon layer these nanoparticles does not oxidized and hydrolyzed when exposed to the air[4]. Nanoparticles have a potential valuable use in the xerographic[5], hyperchromic magnetic resonance imaging contrast agents and agents[6], in the magnetic targeting drug delivery and the magnetic hyperthermia heating tumors[7]. So far, the methods to produce carbon coated materials mainly include: an ion beam method, a biological template method[8], a chemical vapor deposition[9] and an explosion method[10]. All these methods have their own characteristics, but they have several shortcomings, such as carbon arc method is energy consumption and low product purity, the yield of chemical vapor deposition method is low.

In this paper, carbon-coated cobalt nanoparticles are prepared by the starch coating method, a new method to prepare carbon coated nanoparticles. In first step, prepare cobalt nitrate starch complex by sol-gel method, then thermal decompose it under hydrogen atmosphere, finally synthesis of carbon-coated cobalt nanoparticle. Starch in which both as the carbon source and as the cobalt nanoparticles stabilizer. Compared with other methods, this method can be a lot of preparation with low cost.

EXPERIMENTAL

Procedure and precursors: Cobalt(II) nitrate, starch powders and ammonia were used as starting materials. Dissolved starch in ammonia solution, mixed it with $Co(NO_3)_2$ in ethanol solution under agitation. Green brown viscous solution was obtained and dried it at 100 °C for 24 h, cobalt nitrate starch gel was prepared. Then the gel was placed in the tube furnace for pyrolysis. The pyrolysis carbonization process was under the atmosphere of hydrogen, hydrogen flow rate 35 mL/min. Carbonization temperature curve: 10 °C/min, from room temperature to 300 °C. Then to 800 °C with the increase rate of 5 °C/min and keep in 800 °C for 4 h. Natural cooled to room temperature. A black powder-like substance was obtained, these powder are the final products.

Characterization: An X-ray diffraction (XRD) with CuK_α radiation was used at room temperature to identify the phase and the crystal structure .The micro-structure of carbon-coated cobalt nanoparticles was observed by transmission electron microscope (TEM)(JEM-2010 HR) operating at 200 Kv. Magnetic properties at room temperature of the products were characterized by a vibrating sample magnetometer (VSM), at magnetic field of -12-+12 KOe. Q600 DSC/TGA simultaneous, TA companies in the United States was employed to test DSC/TGA. Test conduction: weight between 1.5-2.0 mg, carrier gas is air, heating rate 20 °C/min, from room temperature to 800 °C.

RESULTS AND DISCUSSION

Structural and morphology of carbon-coated cobalt nanoparticles: Fig. 1 is XRD patterns of different content cobalt carbon-coated cobalt nanoparticles, (cobalt content in the sample are 20, 40, 60, and 80 %, respectively) which can be observed from the figure. The products only have carbon and cobalt peaks do not find cobalt carbide and oxide diffraction peaks, indicating carbon-coated cobalt nanoparticles did not contain cobalt oxides and carbides. We found there are not obvious diffraction peaks in the sample of 20 % cobalt content (carbon content 80 %) carbon-coated cobalt nanoparticles, this is due to amorphous carbon in the samples. It is obviously that all the samples have the diffraction peak of cobalt. and with the increase of cobalt content the diffraction intensity increased, the sample of 80 % cobalt content with the strongest (110), (200), (211) diffraction peak (PDF card 06-0696). At the same time we can see that the carbon-coated cobalt nanoparticles of carbon content of 40 % of with a strong carbon peaks, which shows that the sample contains crystalline carbon.

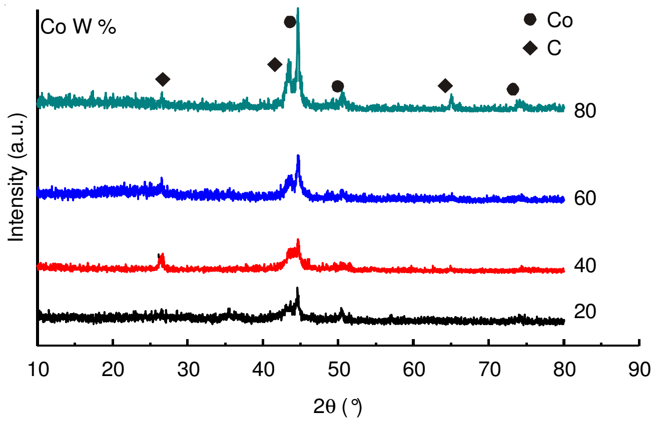

Fig.1. XRD patterns of carbon-coated cobalt nanoparticles

Soluble starch is amylose, molecular formula is $(C_6H_{10}O_5)_n$, in the cobalt/starch gel, The starch powder as a dividers, separate cobalt oxide nanoparticles and in the heating process it prevent the aggregation of cobalt nanoparticles effectively. Heated to about 300 °C, starch start decomposed and finally generated the different types of carbon graphite[11]. Under the cobalt catalystic, these graphite-like materials final formed lamellar graphite and coated on the surface of cobalt nanoparticles.

Fig. 2 shows TEM image of carbon-coated cobalt nanoparticles, which reveal the general morphology, a typical core-shell structure of the nanocapsule materials, nanoparticles are spherical particles with a diameter of 20-40 nm, particle size is fairly uniform. The core (dark part) is metal cobalt, outside (light part) is carbon layers, except carbon-coated cobalt nanoparticles in the specimen, there is a small amount of amorphous carbon particles(the arrows in Fig. 2a, 2b). These amorphous carbon particles, also explained why there is not a strong diffraction peak of carbon in the XRD pattern of the sample which the cobalt content is 20 % (carbon content 80 %).

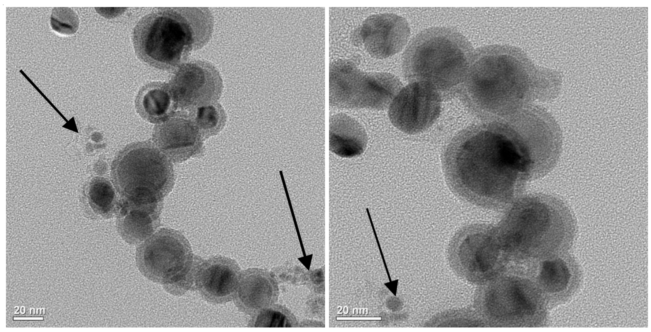

Fig. 2. TEM images of carbon coated cobalt nanoparticles (the arrows point to amorphous carbon)

HRTEM image (Fig. 3) of carbon-coated cobalt nanoparticles, reveals fine structure of these nanocapsules, the thickness of outside carbon layer is 5-10 nm, the cobalt core is about 25 nm in diameter. Carbon layers that close to cobalt core are regular stripes structure, carbon layers that away from the cobalt core are relatively disordered stripes. This is because in the carbonation process cobalt nanoparticles could promote carbon around them be graphite structure, due to the lack of the presence of cobalt catalyst, carbon layers away from cobalt core formed amorphous structure.

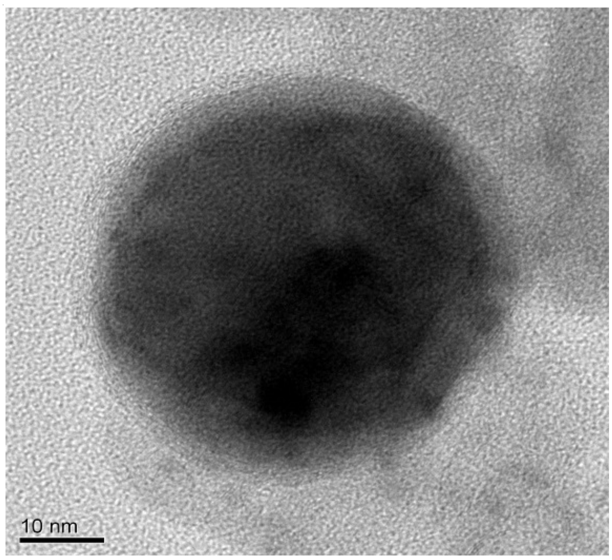

Fig. 3. HRTEM image of carbon coated cobalt nanoparticles

Magnetic property of carbon-coated cobalt nanoparticles: Carbon-coated cobalt nanoparticles as a means of potential applications of magnetic record materials. It is useful to study the magnetic properties of the products. The hysteresis loops at room temperature of carbon coated cobalt nanoparticles (Fig. 4) show the saturation magnetization of samples increase with the increasing of cobalt content, at the same time remanent magnetization and intrinsic coercivity also increase with the cobalt content increase. The magnetic properties of materials could be valued by ratio of remanent and saturation (Mr/Ms). Mr/Ms of the cobalt content of 20 % and 80 % samples is 0.11 and 0.13. Mr/Ms less than 0.25[12] is the soft magnetic materials, so the carbon-coated cobalt nanoparticles is soft magnetic materials.

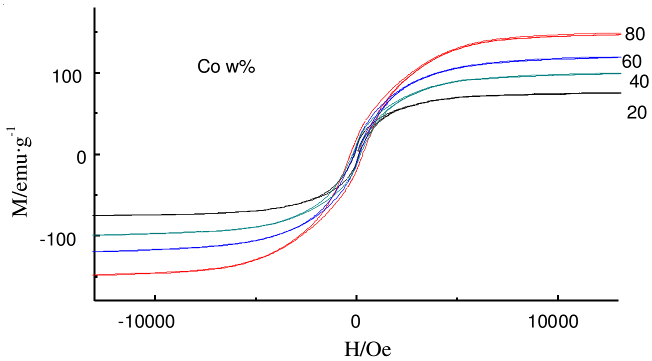

Fig. 4. Magnetic field dependence of magnetization of different coated cobalt nanoparticles

Thermal stability of carbon-coated cobalt nanoparticles: A DSC/TG was employed in order to examine the antioxidant ability, the DSC/TG curves shown in Fig. 5. From the DSC curve, it is clear that there are two exothermic peaks with the increasing of temperature. The two exothermic peaks appeared in 413 °C and 522 °C, respectively, obviously the TG curve can be divided into 3 stages with the temperature increase. From room temperature to 413 °C, sample have a small amount of weight loss, this is the reason for the surface adsorbate evaporation; from 413 to 522 °C, because of the decomposition of amorphous carbon, samples have a greater weight loss. After 522 °C, there are not obvious weight changes, while the exothermic peak in DSC curve of 522 °C is due to a enthalpy occurred in the carbon-coated cobalt nanoparticles. Throughout the period, there is not weight gain phenomenon. This fully shows that the external carbon layers can effectively protect the internal cobalt core from been oxidized.

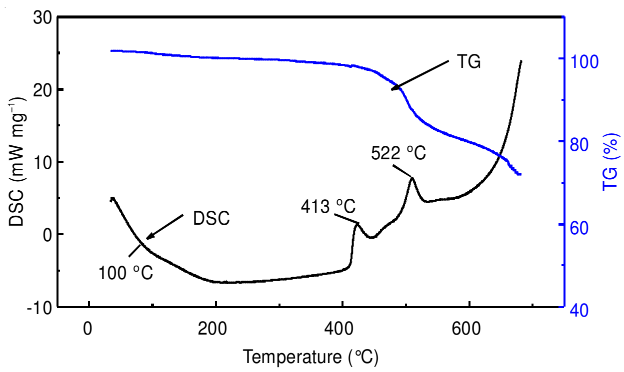

Fig. 5. DSC/TG curve of carbon coated cobalt nanoparticles

Conclusion

Carbon-coated cobalt nanoparticles can be synthesized by the starch coating method. They are spherical particles with the size of particles 20-40 nm in diameter. It is believed that the nanoparticles have a typical core-shell structure with carbon layer outside and cobalt core inside. The oxidation experiment shows that the carbon layers can protect the cobalt core from oxidation. Hysteresis loops show as-made materials have good superparamagnetic properties, with the increase of cobalt content their magnetic properties enhance.

ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of Shaanxi Provincial Department of Education (2010JK676).

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